In-Situ Reaction of Multi-Phase Materials: A New Approach for the Production of Nano/Meso Composite Surface Structures

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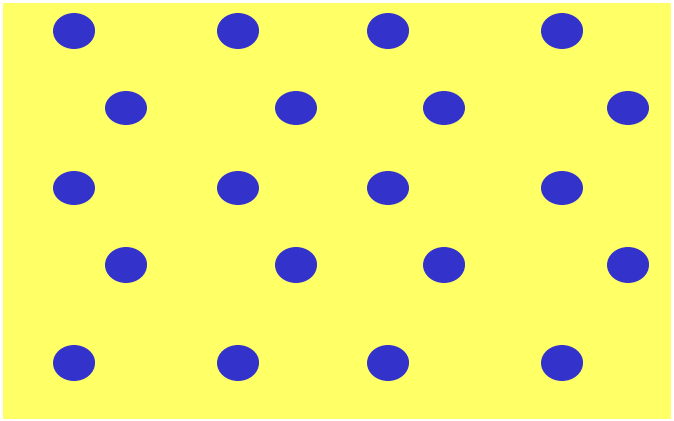
DARPA Meta-Materials Workshop
Sept. 29, 2000

Abstract

We propose to use an obscure form of internal oxidation observed only in multi-phase materials as a basis for a new synthesis approach for the production of novel functional alloy-phase dispersed ceramic composite structures on a nano/meso scale. The potential advantage of this approach is the opportunity to tailor the size, spatial distribution, and chemistry of the structure with a greater degree of precision than currently available techniques. Because this phenomenon is effectively a self-organizing process, the potential exists for coverage of large surface areas in an economical manner.

Metal + Ceramic Nano/Meso Composites Exhibit Unique and Potentially Useful Properties



Metal Phase (1-100 nm)
Ceramic (Oxide, Nitride, etc.)

- Enhanced Coercivity: eg. Ni in SiO_2, Fe in SiO_2 (Roy et al., 1993)
- Giant Magnetoresistance: eg. Co in Al_2O_3 (Fujimori et al., 1996)
- Nonlinear Optical Properties: ex. Cu in SiO_2 (Haglund et al., 1993)

Potential Applications Include Magnetic Recording Media, Optical Switches, Gas Sensors, Fuel Cells, Many Others...

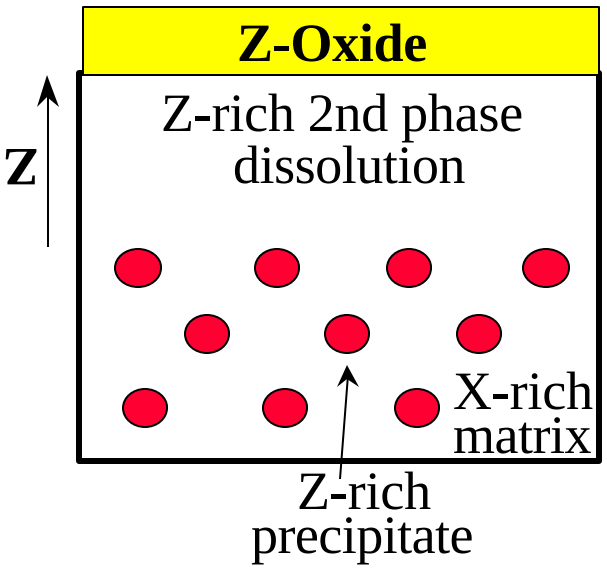
Limited Chemical and Spatial Control With Conventional Synthesis Techniques

(e.g. Ion implantation, Sol-gel, Sputtering)

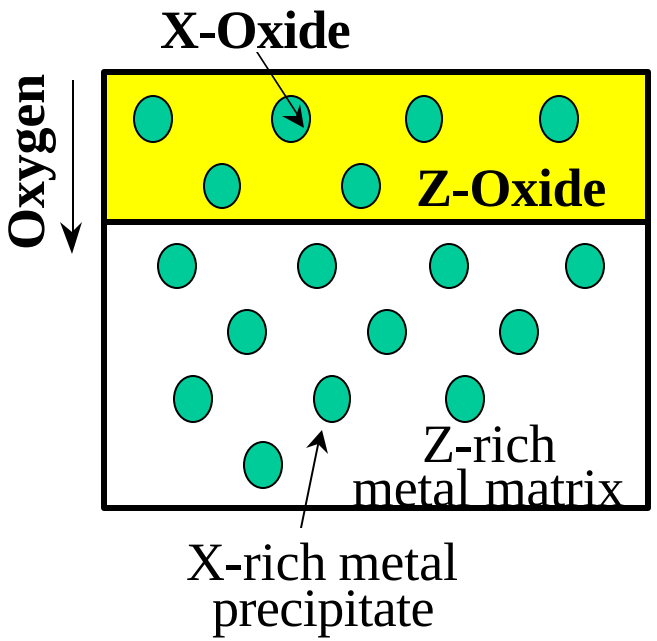
- **Elemental**-Metal Dispersions Achievable: eg. Fe in SiO_2
- Don't Readily Lend Themselves to **Alloy** Metal Phases: eg. Fe-Co Solid Solution or Fe_3Ni in SiO_2 (Needed to tailor and optimize properties for a given device/application)
- Limited Control of Metal Phase Spatial Arrangement

New Techniques and/or Approaches Needed
Must be Economical!

Two Limiting Cases for Oxidation of Two-Phase Alloys



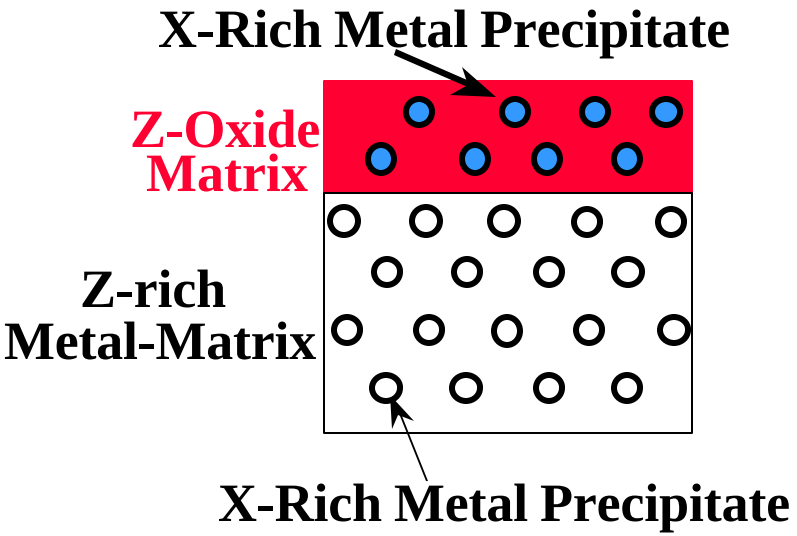
Cooperative Mode

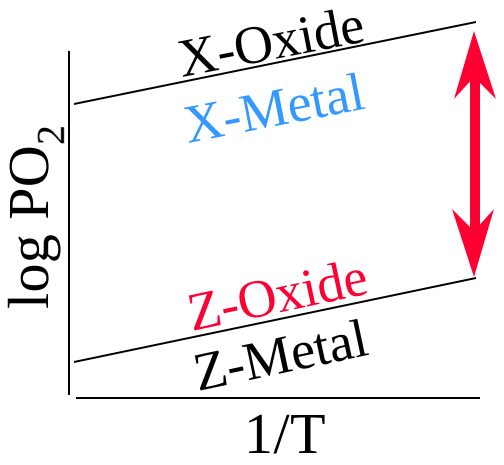


Independent Mode

- Cooperative: Single-Phase Reaction Product, Desirable for Metal Protection in Aggressive High-Temperature Environments
- Independent: Composite Surface Which Mimics Underlying Alloy Structure, **Very Obscure**, Undesirable for Metal Protection, Not Viewed as Useful, **BUT...**

Independent Mode of Internal Oxidation Holds Great Promise as a New Synthesis Approach to Nano/Meso Composite Surface Structures



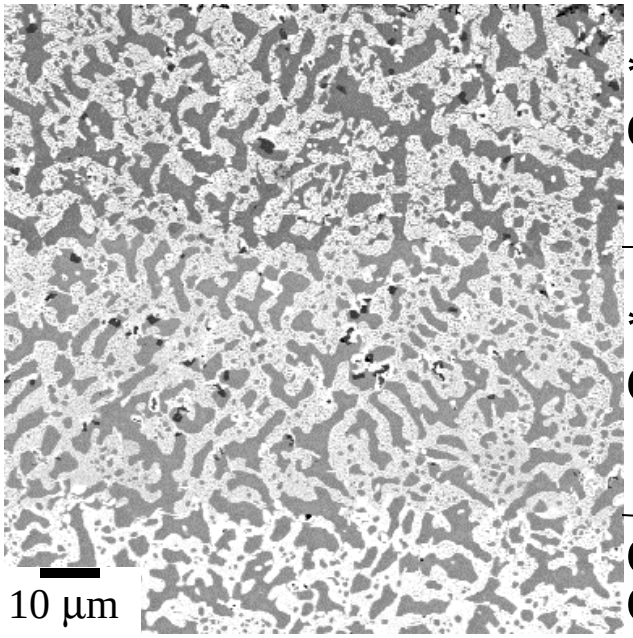


- Selectively Oxidize Matrix Phase Only by Control of Oxidant Partial Pressure (component elements of dispersed alloy phase more noble than those of matrix phase)

- Applicable to Oxidation, Nitridation, Carburization, etc.

Independent Internal Nitridation Mimics Underlying Structure of a Bulk Cast Two-Phase $Cr+Cr_2Nb$ Alloy

SEM Cross-Section Micrograph



*Cr_2NbN (light gray)
Cr_2N (dark)

*Cr_2NbN (light gray)
Cr metal (dark)

Cr_2Nb metal (white)
Cr metal (dark)

- Initial Alloy Structure Acts as a Template and Organizes the Size, Spatial Distribution, and Chemistry of the Resultant Composite Nitride Structure

*Composition stoichiometry only based on electron microprobe analysis

Proposed Synthesis Approach

Deposit Selected Thin Film Composition or Utilize Surface of Bulk Alloy

↓

Thermal Treatment to Produce a Two-Phase Metallic Nano/Meso Structure Via Solid State Precipitation Reactions (leverages versatile alloy phase equilibria to control structure)

↓

Select Oxidant Partial Pressure So That Component Elements of Matrix Phase Will Oxidize But Those of Second Phase Dispersion Will Not

↓

Select Conditions Which Promote Independent Internal Oxidation to Selectively Convert Matrix to Ceramic and Encapsulate Second Phase Alloy Precipitate

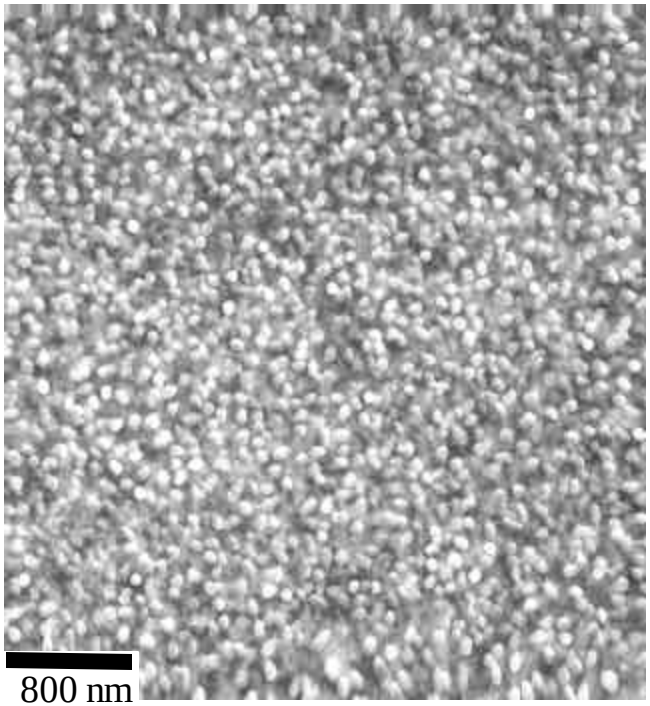
What's New?

- Recognition and Utilization of Unique Two-Phase Alloy Oxidation Phenomenon to Synthesize Composite Surface

- Use of Alloy Phase Equilibria to Provide Superior Control of the Size, Spatial Distribution, and Chemistry of the Metallic Dispersion

Nanocomposite Synthesis by Oxidation of a Two-Phase Alloy Precursor Appears Possible

Oxidation of a Vapor Deposited Si-Ag Thin Film Yields 75-100 nm Ag "Balls" (Light) Dispersed in SiO_2 (Dark)



- Si-Ag: Simple Binary Immiscible System (no precipitation reaction to control initial structure)
- Proposed work will attempt to control structure by utilizing precipitation reactions in more complex alloy systems

Summary of Key Aspects

- Internal Oxidation of a Two-Phase Alloy as a Synthesis Technique
- Yields Dispersed Alloy Phase in a Ceramic Matrix (not limited to elemental dispersions: e.g. Co in Al_2O_3)
- Can Modify Bulk Alloy Surface or Use Deposited Thin Film
- Control of Oxidant Partial Pressure Allows Selective Oxidation of Matrix Phase